

## DESCRIPTION

### METHOD FOR PRODUCING Ti OR Ti ALLOY THROUGH REDUCTION BY Ca

#### 5 TECHNICAL FIELD

[0001] The present invention relates to a method for producing Ti or Ti alloys through reduction by Ca, in which a metallic chloride containing titanium tetrachloride (TiCl<sub>4</sub>) is reduced by Ca to produce Ti metals or Ti alloys.

#### 10 BACKGROUND ART

[0002] A Kroll method for reducing TiCl<sub>4</sub> by Mg is generally used as an industrial production method of the titanium metals. In the Kroll method, the Ti metals are produced through a reduction step and a vacuum separation step. In the reduction step, TiCl<sub>4</sub> which is of a raw material of Ti is reduced in a reactor vessel to produce the sponge metallic Ti. In the vacuum separation step, unreacted Mg and magnesium chloride (MgCl<sub>2</sub>) formed as by-products are removed from the sponge metallic Ti produced in the reactor vessel.

[0003] The reduction step will be described in detail. In this step, the reactor vessel is filled with the molten Mg, and the TiCl<sub>4</sub> liquid is supplied from above on a liquid surface of the molten Mg. This allows TiCl<sub>4</sub> to be reduced by Mg near the liquid surface of the molten Mg to generate the particulate metallic Ti. The generated Ti metals move sequentially downward. At the same time, the molten MgCl<sub>2</sub> which is of the by-product is generated near the liquid surface. A specific gravity of molten MgCl<sub>2</sub> is larger than that of the molten Mg. The molten MgCl<sub>2</sub> which is of the by-product moves downward due to the specific-gravity difference, and the molten Mg emerges in the liquid surface instead. The molten Mg is continuously supplied to the liquid surface by the specific-gravity difference substitution, and the reducing reaction of TiCl<sub>4</sub> proceeds continuously.

[0004] In the Ti metal production by the Kroll method, a high-purity product is produced. However, a production cost is increased and the product becomes remarkably expensive. One of factors of increased production cost is the difficulty in enhancing a feed rate of  $TiCl_4$ . The following three items are cited 5 as the reason why the feed rate of  $TiCl_4$  is restricted.

[0005] In order to improve productivity in the Kroll method, it is effective to increase the feed rate of  $TiCl_4$  which is of the raw material of Ti, i.e., to increase a supply amount of molten Mg to the liquid surface per unit area or unit time. However, when the feed rate of  $TiCl_4$  is excessively increased, the 10 specific-gravity difference substitution cannot keep up with the reaction rate, so that while  $MgCl_2$  remains in the liquid surface,  $TiCl_4$  is supplied to the  $MgCl_2$ . As a result, the supplied  $TiCl_4$  becomes lower grade chloride gases (referred to as "unreacted gas") such as an unreacted  $TiCl_4$  gas and a  $TiCl_3$  gas, and the unreacted gas is discharged outside the reactor vessel, which reduces 15 utilization efficiency of  $TiCl_4$ . It is necessary to avoid the generation of the unreacted gas, because a rapid increase in inner pressure of the reactor vessel is associated with the generation of the unreacted gas. Thus, there is a limit of the feed rate of  $TiCl_4$  because of the above reasons.

[0006] When the feed rate of  $TiCl_4$  is enhanced, Mg vapor generated from the 20 liquid surface of the molten Mg reacts with  $TiCl_4$  vapor to increase a precipitation amount of Ti in the inner surface of the reactor vessel above the liquid surface of the molten Mg. On the other hand, the liquid surface of the molten Mg rises as the reducing reaction proceeds. Therefore, the precipitated 25 Ti in the inner surface of the upper portion of the reactor vessel is immersed in the molten Mg at a late stage of the reducing reaction, which causes the effective area of the Mg liquid surface to be decreased to reduce the reaction rate. In order to suppress the decrease of reaction rate, it is necessary that the feed rate of  $TiCl_4$  be restricted to prevent the Ti precipitation in the inner surface of the upper portion of the reactor vessel.

[0007] Therefore, Japanese Patent Application Publication No. 8-295955 proposes a method in which the reaction efficiency is enhanced by supplying liquid  $TiCl_4$  in a dispersive manner to the liquid surface in which the molten Mg exists, and thereby the Ti precipitation is suppressed in the inner surface of the upper portion of the reactor vessel. However, the method proposed in Japanese Patent Application Publication No. 8-295955 is not enough to suppress the Ti precipitation. In the Kroll method, because the reaction is performed only near the liquid surface of the molten Mg in the reactor vessel, an exothermic area is narrowed and the temperature is locally elevated.

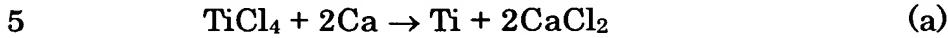
10 Therefore, cooling becomes difficult, so that the feed rate of  $TiCl_4$  is restricted.

[0008] Although the feed rate of  $TiCl_4$  is not directly affected, in the Kroll method, Ti is generated in the particulate form near the liquid surface of the molten Mg liquid, and moves downward. However, because of wetting properties (adhesion properties) of the molten Mg, the generated Ti powder moves downward while aggregated, and the Ti particles are sintered to grow the Ti particles in size by the temperature condition of the molten liquid during moving downward, which makes it difficult to discharge the Ti particles outside the reactor vessel. Therefore, the continuous production is difficult to perform, and the improvement of the productivity is blocked. This is the reason why

15 the Ti is produced in the batch manner in the form of the sponge titanium by the Kroll method.

[0009] With reference to the Ti production methods except for the Kroll method, for example, US Patent No. 2205854 describes that, in addition to Mg, for example, Ca can be used as the reducing agent of  $TiCl_4$ . US Patent No. 25 4820339 describes a method for producing Ti through the reducing reaction by Ca, in which the molten salt of  $CaCl_2$  is held in the reactor vessel, the metallic Ca powder is supplied into the molten salt from above, Ca is dissolved in the molten salt, and  $TiCl_4$  gas is supplied from below to react the dissolved Ca with  $TiCl_4$  in the molten salt of  $CaCl_2$ .

[0010] In the reduction by Ca, the Ti metals are generated from  $\text{TiCl}_4$  by the reaction of the following chemical formula (a), and  $\text{CaCl}_2$  as the by-product is also generated at the same time. Ca has a stronger affinity for Cl stronger than Mg has, and Ca is suitable for the reducing agent of  $\text{TiCl}_4$  in principle.



[0011] Particularly, in the method described in US Patent No. 4820339, Ca is used while dissolved in the molten  $\text{CaCl}_2$ . When the reducing reaction by Ca is utilized in the molten  $\text{CaCl}_2$ , a reaction field is enlarged compared with the Kroll method in which  $\text{TiCl}_4$  is supplied to the liquid surface of the reducing agent in the reactor vessel and the reaction field is limited to near the liquid surface. Therefore, because the exothermic area is also enlarged to facilitate the cooling, the feed rate of  $\text{TiCl}_4$  which is of the raw material of Ti can be largely increased, and the remarkable improvement of the productivity can be also expected.

10 [0012] However, it is difficult that the method described in US Patent No. 4820339 is adopted as the industrial Ti production method. When using the metallic Ca powder as the reducing agent, since the metallic Ca powder is extremely expensive, the production cost is higher than that of the Kroll method in which the feed rate of  $\text{TiCl}_4$  is restricted. In addition, the highly reactive Ca is extremely difficult to handle, which can also be the factor of blocking the industrial application of the method for producing Ti through the reduction by Ca.

15 [0013] An example of other Ti production methods includes an Olsen method described in US Patent No. 2845386. The Olsen method is a kind of oxide direct-reduction method for directly reducing  $\text{TiO}_2$  by Ca, in which  $\text{TiO}_2$  is directly reduced by Ca, not through  $\text{TiCl}_4$ . Although the oxide direct-reduction method is highly efficient, the oxide direct-reduction method is not suitable for the production of the high-purity Ti because it is necessary to use high-purity  $\text{TiO}_2$ .

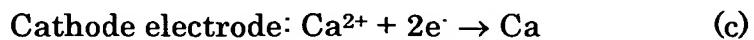
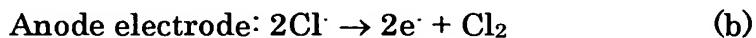
## DISCLOSURE OF THE INVENTION

[0014] It is an object of the present invention to provide a method for economically producing high-purity Ti metals or high-purity Ti alloys with high efficiency without using an expensive reducing agent.

[0015] In order to achieve the above object, the present inventors consider that  $TiCl_4$  be reduced by Ca, and the present inventors look into the method for utilizing Ca dissolved in the molten salt of  $CaCl_2$  described in US Patent No. 4820339.

10           In the method described in US Patent No. 4820339, Ca in the molten salt is consumed in the reducing reactor vessel as the reaction expressed by the chemical formula (a) proceeds, and it is necessary to continuously supply the metallic Ca powder to the reducing reactor vessel. However, in order to industrially establish the method for producing Ti through reduction by Ca, the 15 present inventors focus on a method for controlling a dissolved Ca concentration in the molten salt by electrolysis in consideration of the fact that it is necessary that the Ca consumed in the reducing reaction is economically replenished into the molten salt.

[0016] That is, when the molten  $CaCl_2$  is electrolyzed in a reactor cell, 20 electrode reactions expressed by the following chemical formulas (b) and (c) proceed to generate a  $Cl_2$  gas near the surface of an anode electrode while generating Ca near the surface of a cathode electrode, which allows the Ca concentration to be increased in the molten salt. Therefore, when  $TiCl_4$  is supplied to  $CaCl_2$  so as to react with Ca generated on the anode electrode side, 25 because Ca consumed in the Ti generation is replenished as needed, the replenishment of metallic Ca from the outside or extraction of metallic Ca becomes unnecessary, which allows the Ti metals to be economically produced.



[0017] The method for replenishing Ca consumed by the reduction of  $TiCl_4$  with Ca generated by the electrolysis can also be achieved by respectively performing the reduction and the electrolysis in a reducing cell and an electrolytic cell to circulate the molten  $CaCl_2$  between the cells. However, 5 when  $TiCl_4$  is supplied to the molten  $CaCl_2$  in the reactor cell so as to react with Ca generated on the cathode electrode side by the electrolysis, the reactor cell can commonly be used as the reducing cell and the electrolytic cell. Therefore, because it is not necessary to separately provide the reducing cell and the electrolytic cell, there is a great advantage from a viewpoint of installation cost 10 compared with the case in which the molten  $CaCl_2$  is circulated between the reducing cell and the electrolytic cell.

[0018] The present invention is made based on the above consideration, and the summary of the present invention is a method for producing Ti or Ti alloys through reduction by Ca according to the following (1) to (7).

15 (1) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the molten salt containing  $CaCl_2$  while Ca being dissolved in the molten salt and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride 20 containing  $TiCl_4$  into the molten salt in order to cause the metallic chloride containing  $TiCl_4$  to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell, in which the reactor cell is provided with a membrane which partitions an inside of the 25 reactor cell into an anode electrode side and the cathode electrode side, the membrane blocking the movement of Ca generated on the cathode electrode side in the reactor cell to the anode electrode side while permitting the molten salt to flow in the reactor cell (hereinafter referred to as "production method described in (1)").

[0019] (2) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis using an electroconductive porous material as an cathode electrode in the molten salt of the reactor cell, the molten salt containing  $\text{CaCl}_2$  while Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing  $\text{TiCl}_4$  into the molten salt through the cathode electrode in order to cause the metallic chloride containing  $\text{TiCl}_4$  to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell (hereinafter referred to as "production method described in (2)").

[0020] (3) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the molten salt containing  $\text{CaCl}_2$  while Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing  $\text{TiCl}_4$  into the molten salt in order to cause the metallic chloride containing  $\text{TiCl}_4$  to react with Ca generated on a cathode electrode side by the electrolysis; a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell; and a chlorination step of causing  $\text{Cl}_2$  to react with  $\text{TiO}_2$  to generate  $\text{TiCl}_4$ ,  $\text{Cl}_2$  being generated on an anode electrode side in association with the electrolysis, in which  $\text{TiCl}_4$  generated in the chlorination step is used for the Ti or Ti alloy generation reaction in the reactor cell (hereinafter referred to as "production method described in (3)").

[0021] (4) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the molten salt containing  $\text{CaCl}_2$  while Ca being dissolved in the molten salt, and

Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing  $TiCl_4$  into the molten salt in order to cause the metallic chloride containing  $TiCl_4$  to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step in which Ti or Ti alloys generated in the reactor cell are extracted to an outside of the reactor cell along with the molten salt and the Ti or Ti alloys are separated from the molten salt outside the reactor cell (hereinafter referred to as "production method described in (4)").

5 [0022] (5) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a multi-system molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the multi-system molten salt containing at least one of  $NaCl$ ,  $KCl$ ,  $LiCl$ , and  $CaF_2$  in addition to  $CaCl_2$ , Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing  $TiCl_4$  into the molten salt in order to cause the metallic chloride containing  $TiCl_4$  to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell (hereinafter referred to as "production method described in (5)").

10 [0023] (6) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt in the reactor cell, the molten salt containing  $CaCl_2$  while Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a mixed gas containing  $TiCl_4$  and another metallic chloride into the molten salt in order to cause the mixed gas to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell (hereinafter referred to as "production method described in (6)").

15 [0024] (7) A method for producing Ti or Ti alloys through reduction by Ca,

including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the molten salt containing  $\text{CaCl}_2$  while  $\text{Ca}$  being dissolved in the molten salt, and  $\text{Ti}$  or  $\text{Ti}$  alloys are generated in the molten salt by supplying a metallic chloride containing  $\text{TiCl}_4$  into the molten salt in order to cause the metallic chloride containing  $\text{TiCl}_4$  to react with  $\text{Ca}$  generated on a cathode electrode side by the electrolysis, said  $\text{Ti}$  or  $\text{Ti}$  alloys being formed in powder whose average particle size ranging from 0.5 to 50  $\mu\text{m}$ ; and a  $\text{Ti}$  separation step of separating the  $\text{Ti}$  or  $\text{Ti}$  alloys from the molten salt inside the reactor cell or outside the reactor cell (hereinafter referred to as "production method described in (7)").

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0025] Fig. 1 is a view showing a relationship between a mixture ratio and a melting point in a binary system mixed molten salt of  $\text{CaCl}_2$  and  $\text{NaCl}$ ;

15 Fig. 2 is a block diagram showing a  $\text{Ti}$  metal production apparatus to which a first embodiment mode according to the present invention can be applied;

20 Fig. 3 is a block diagram showing a  $\text{Ti}$  metal production apparatus to which a second embodiment mode according to the present invention can be applied; and

Fig. 4 is a block diagram showing a  $\text{Ti}$  metal production apparatus to which a third embodiment mode according to the present invention can be applied.

#### 25 BEST MODE FOR CARRYING OUT THE INVENTION

[0026] 1. Contents of the Method according to the Invention (Production Methods Described in (1) to (7))

In each of the methods according to the present invention for producing  $\text{Ti}$  or  $\text{Ti}$  alloys through the reduction by  $\text{Ca}$ , for example, the molten

CaCl<sub>2</sub> which is of the molten salt is held in the reactor cell. When TiCl<sub>4</sub> is supplied to the molten salt in the reactor cell, TiCl<sub>4</sub> is reduced by Ca dissolved in the molten salt, and the particulate and/or powdery metallic Ti (hereinafter referred to as "Ti particles") is generated. Although Ca dissolved in the molten salt is consumed in association with the generation of the Ti particles, because the electrolysis of the molten CaCl<sub>2</sub> progresses in conjunction with the reducing reaction in the reactor cell, Ca is generated on the cathode electrode side and the dissolved Ca which is consumed in the reducing reaction is replenished with Ca generated by the electrolysis. Therefore, the metallic Ca replenishment operation and the metallic Ca extraction operation are not required while the Ti particles are continuously produced.

[0027] Conventionally one of the main reasons why Ca is not used in the industrial production of the Ti metals is the difficulty in separating Ca and CaCl<sub>2</sub>. Mg is produced by electrolyzing MgCl<sub>2</sub>, and the generated Mg can efficiently be recovered because Mg is hardly dissolved in MgCl<sub>2</sub>. Similarly to Mg, Na can efficiently be produced by electrolyzing NaCl. On the other hand, Ca is produced by electrolyzing CaCl<sub>2</sub>, and the generated Ca is dissolved in CaCl<sub>2</sub> by about 1.5%.

[0028] Therefore, it is difficult to efficiently produce only Ca. In addition, there is also a phenomenon in which the dissolved Ca generates CaCl<sub>2</sub> by a back reaction (reaction in which Ca generated on the cathode electrode side is bonded to Cl<sub>2</sub> generated on the anode electrode side to return to CaCl<sub>2</sub>), so that the production efficiency of Ca becomes worsened. For example, the improvement of a recovery factor of Ca is performed by cooling an electrode. However, the production cost of Ca is still high.

However, in the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, Ca dissolved in the molten CaCl<sub>2</sub> is used and the Ca separation is not required, so that the Ca electrolytic production cost can be decreased.

[0029] When the Ca reduction in the molten salt is utilized, the reducing reaction field is expanded and the heat generation area is simultaneously enlarged. Mg has vapor pressure of 6.7 kPa (50 mmHg) at 850 °C while Ca has extremely small vapor pressure of 0.3 kPa (2 mmHg). Therefore, in the 5 case where Ca is used for the reduction process, the Ti precipitation amount becomes dramatically lessened in the inner surface of the upper portion of the reactor cell when compared with the use of Mg. Accordingly, in the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, the TiCl<sub>4</sub> feed rate can be largely increased.

10 In addition, Ca is inferior in wetting properties (adhesion properties) to Mg, and Ca adhering to the precipitated Ti particles is dissolved in CaCl<sub>2</sub>, so that the particle growth caused by the aggregation and the sintering in the generated titanium particles are significantly lessened. Therefore, the generated Ti can be discharged in the form of particles from the reactor cell, 15 and the Ti production can continuously be operated.

[0030] For a supply mode of TiCl<sub>4</sub> to the molten CaCl<sub>2</sub> liquid, it is particularly desirable that TiCl<sub>4</sub> be directly supplied in the gas state into the molten CaCl<sub>2</sub> liquid because of higher contact efficiency of TiCl<sub>4</sub> with Ca in the molten CaCl<sub>2</sub> liquid. However, the TiCl<sub>4</sub> supply mode is not limited to the one 20 in which TiCl<sub>4</sub> in the gas state is supplied. For example, it is also possible that either the liquid or gaseous TiCl<sub>4</sub> is supplied to the liquid surface of the molten CaCl<sub>2</sub> liquid, or it is also possible that either the liquid or gaseous TiCl<sub>4</sub> is supplied to either the liquid surface or the inside of the molten Ca liquid held on the molten CaCl<sub>2</sub> liquid.

25 [0031] In the case where the reducing reaction is generated by supplying the TiCl<sub>4</sub> liquid to the surface of the molten Ca liquid held on the molten CaCl<sub>2</sub> liquid, it is desirable that the molten Ca liquid be held in a thin state to an extent in which Ca in the molten CaCl<sub>2</sub> liquid can be utilized. When the Ca layer is thin, because Ca in the molten CaCl<sub>2</sub> liquid is involved in the reaction,

the reaction can range from the molten Ca layer to the molten  $\text{CaCl}_2$  layer to continue the Ti generation even if the specific gravity difference substitution becomes unable to keep up with it due to the increase in the  $\text{TiCl}_4$  feed rate.

5 [0032] For the supply of  $\text{TiCl}_4$  gas, the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention has various advantages compared with the Kroll method.

That is, in the Kroll method, the  $\text{TiCl}_4$  liquid is supplied to the liquid surface of the molten Mg liquid, and it has been tried that the  $\text{TiCl}_4$  gas is supplied into the molten Mg liquid in order to enlarge the reaction field. 10 However, as described above, since the Mg has the large vapor pressure, the Mg vapor intrudes in a supply nozzle to react with  $\text{TiCl}_4$ , and the supply nozzle is choked.

15 [0033] Meanwhile, it has been tried that the  $\text{TiCl}_4$  gas is supplied into the molten  $\text{MgCl}_2$  liquid. However, the nozzle choking problem still remains although a choking frequency of the supply nozzle is decreased. This is because sometimes the melt is stirred by the bubbling of the  $\text{TiCl}_4$  gas to cause the molten Mg to reach the supply nozzle. Even if  $\text{TiCl}_4$  is supplied to the molten  $\text{MgCl}_2$  liquid, the reducing reaction is difficult to occur because Mg is hardly dissolved in the melt.

20 [0034] On the contrary, in the method of utilizing the Ca reduction, the nozzle choking is hardly generated, and the  $\text{TiCl}_4$  gas can be supplied into the molten  $\text{CaCl}_2$  liquid. The reason why the nozzle choking is hardly generated is attributed to the fact that the molten Ca has the small vapor pressure.

25 That is, the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, it is particularly desirable that  $\text{TiCl}_4$  be directly supplied in the gas state to the molten  $\text{CaCl}_2$  liquid, and this supply mode can be applied without any problem in the actual operation. It is also possible to adopt the supply mode in which either the liquid or gaseous  $\text{TiCl}_4$  is supplied to the liquid surface of the molten  $\text{CaCl}_2$  liquid or to the liquid

surface or the inside of the molten Ca liquid held on the molten  $\text{CaCl}_2$  liquid.

[0035] In the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, the Ti particles generated in the molten  $\text{CaCl}_2$  liquid can be separated from the molten  $\text{CaCl}_2$  liquid either in the reactor

5 cell or outside the reactor cell.

However, when the separation is performed in the reactor cell, the production mode becomes the batch manner. In order to improve the productivity, the Ti particles and the molten  $\text{CaCl}_2$  liquid can be separated from each other outside the reactor cell by utilizing the Ti generated in the 10 particulate form to discharge the Ti particles outside the reactor cell along with the molten  $\text{CaCl}_2$  liquid. This step is included as the Ti separation step in the production method described in (4). According to the production method described in (4), the Ti particles can simply be separated from the molten salt by a squeezing operation by means of mechanical compression.

15 [0036] For handling  $\text{Cl}_2$  generated by the electrolysis, as stipulated by the production method described in (3), desirably  $\text{Cl}_2$  is caused to react with  $\text{TiO}_2$  to generate  $\text{TiCl}_4$ , and the  $\text{TiCl}_4$  is used for the Ti or Ti alloy generation reaction in the reactor cell.

[0037] In the case where Ti is produced by the method according to the 20 present invention,  $\text{TiCl}_4$  is used as the raw material. However, the Ti alloy can also be produced by mixing  $\text{TiCl}_4$  and other metallic chloride. Because  $\text{TiCl}_4$  and other metallic chloride are simultaneously reduced by Ca, the Ti alloy particles can be produced by this method.

[0038]  $\text{TiCl}_4$  and other metallic chloride may be used in either the gas state 25 or the liquid state. However, as stipulated by the production method described in (6), because of higher contact efficiency of  $\text{TiCl}_4$  with Ca in the molten  $\text{CaCl}_2$  liquid, desirably  $\text{TiCl}_4$  and other metallic chloride are used in the mixed gas containing  $\text{TiCl}_4$  and other metallic chloride is used.

[0039] In the method according to the present invention for producing Ti or

Ti alloys through the reduction by Ca, there are problems such as the back reaction and the reactor material wastage. In the back reaction, Ca (Ca generated on the cathode electrode side or the unreacted Ca) in the molten  $\text{CaCl}_2$  are bonded to  $\text{Cl}_2$  generated on the anode electrode side, and Ca returns 5 to  $\text{CaCl}_2$ . The reactor material wastage is caused by the high reactivity of Ca. When the back reaction is generated, the current efficiency is decreased because the electrolytic current is consumed for the back reaction.

As stipulated by the production method described in (1), the back reaction problem, particularly the back reaction in which Ca generated on the 10 cathode electrode side is bonded to  $\text{Cl}_2$  generated on the anode electrode side can effectively be suppressed by using a reactor cell including a membrane which partitions the electrolytic cell into the anode electrode side and the cathode electrode side. The reactor cell holds the molten salt, and the membrane permits the molten salt to be circulated in the electrolytic cell while 15 blocking the movement of Ca generated on the cathode electrode side to the anode electrode side in the reactor cell.

[0040] On the other hand, to address the problem of the reactor material wastage, it is effective that the molten salt is not formed by the single  $\text{CaCl}_2$  but formed by a mixed salt so that a melting point of the molten salt is decreased to 20 lower the molten salt temperature (namely bath temperature). That is, as stipulated by the production method described in (5), usually  $\text{CaCl}_2$  having the melting point of 780 °C is used as the molten salt. However, like binary molten salts such as  $\text{CaCl}_2\text{-NaCl}$  and  $\text{CaCl}_2\text{-KCl}$  and ternary molten salts such as  $\text{CaCl}_2\text{-NaCl-KCl}$ , at least one of other salts (for example,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{LiCl}$ , 25 and  $\text{CaF}_2$ ) can be mixed into  $\text{CaCl}_2$  to form a multi-system molten salt.

This enables the melting point of the salt to be decreased to lower the molten salt temperature. As a result, a life of the reactor material can be lengthened, the reactor material cost can be reduced, and the Ca or salt vaporization from the liquid surface can also be suppressed.

[0041] The mixed molten salt in which NaCl is added to CaCl<sub>2</sub> particularly needs care among the multi-system molten salts.

Fig. 1 shows a relationship between a mixture ratio and a melting point in the binary molten salt of CaCl<sub>2</sub> and NaCl. The melting point of CaCl<sub>2</sub> is singly about 780 °C, while the melting point of NaCl is singly about 800 °C. However, when CaCl<sub>2</sub> and NaCl are mixed together, the melting point is decreased to about 500 °C at the minimum. The melting point of the mixed salt becomes not more than 600 °C when the mixture ratio of NaCl ranges from about 20% to about 45%.

[0042] In the multi-system mixed molten salt such as CaCl<sub>2</sub>·NaCl and CaCl<sub>2</sub>·NaCl·KCl containing CaCl<sub>2</sub> and NaCl, as shown in the following chemical formulas (d) and (e), there is a critical phenomenon in which Ca is generated at temperatures not more than 600 °C while Na is generated at temperatures more than 600 °C. That is, even if CaCl<sub>2</sub> is mixed in NaCl to lower the molten salt temperature to be at temperatures more than 600 °C, Ca is not generated but Na is generated in the molten salt, and the reducing reaction by Ca does not proceed.

Therefore, in the case where the molten salt temperature is decreased by mixing the NaCl with CaCl<sub>2</sub>, NaCl is mixed such that the molten salt temperature becomes not more than 600 °C, and it is necessary to manage the molten salt at the temperatures not more than 600 °C.



[0043] As described above, it should be careful that the restriction in use exists in the multi-system molten salt containing CaCl<sub>2</sub> and NaCl. In the meantime, the critical phenomenon is desirable from the viewpoint of reactor material protection because the large decrease in molten salt temperature can be realized. In addition, the critical phenomenon effectively suppresses the back reaction, particularly the back reaction in which the unreacted Ca is

bonded to  $\text{Cl}_2$  generated on the anode electrode side and Ca returns to  $\text{CaCl}_2$ .

Specifically, in the case where the Ti particles generated on the cathode electrode side in the reactor cell is separated from the molten salt, as described above, from the view point of operation, it is rational that the Ti 5 particles are extracted to the outside of the cell along with the molten salt after use and the Ti particles are separated from the molten salt outside the cell. In this case, usually the molten salt separated from the Ti particles is returned onto the anode electrode side in the reactor cell, the molten salt contains the unreacted Ca although the molten salt is already used, which results in the 10 back reaction.

[0044] However, the unreacted Ca in the molten salt is replaced by Na through the reaction of the chemical formula (e), when the molten salt having the temperature not more than 600 °C extracted from the cathode electrode side in the reactor cell is temporarily heated more than 600 °C outside the 15 reactor cell before the molten salt is returned to the anode electrode side in the reactor cell. Unlike Ca, Na is not dissolved in the molten salt but Na is separated from the molten salt, so that Na can be separated and removed from the molten salt.

Therefore, when the molten salt is returned to the cathode electrode 20 side in the reactor cell after Na is separated and removed, even if the molten salt temperature is lowered to 600 °C or less on the anode electrode side in the reactor cell, the reaction of the chemical formula (d) does not progress to block the Ca regeneration because Na is removed.

[0045] That is, in the multi-system molten salt containing  $\text{CaCl}_2$  and  $\text{NaCl}$ , 25 Ca is dissolved in the molten salt while Na is not dissolved in the molten salt. When the molten salt temperature exceeds 600 °C, Na is generated instead of Ca. When the two phenomena are combined, the unreacted Ca contained in the molten salt after use can be decreased to effectively suppress the back reaction caused by the unreacted Ca and the decrease in current efficiency.

[0046] As stipulated by the production method described in (7), desirably the average size of the generated Ti particles of Ti alloy particles ranges from 0.5 to 50  $\mu\text{m}$ . After the Ti or Ti alloy particles are generated in the molten salt, the Ti or Ti alloy particles are extracted from the reactor cell along with the molten salt, and the Ti or Ti alloy particles are separated from the molten salt. The Ti or Ti alloy particles having the sizes not more than 50  $\mu\text{m}$  can be fluidized along with the molten salt. When the particle size is more than 50  $\mu\text{m}$ , it is difficult that the Ti or Ti alloy particles are extracted from the reactor cell along with the molten salt. Unless the Ti or Ti alloy particles are not less than 0.5  $\mu\text{m}$ , it is difficult that the Ti or Ti alloy particles are separated from the molten salt after the extraction.

[0047] 2. Embodiment modes of Method according to the Invention

Embodiment modes of the present invention will be described below with reference to the drawing.

Fig. 2 is a block diagram showing a Ti metal production apparatus to which a first embodiment mode of the present invention can be applied.

A reactor cell 1 in which the reducing reaction and the electrolytic reaction concurrently occur is used in the first embodiment mode. The reactor cell 1 holds the Ca-rich molten  $\text{CaCl}_2$  in which the relatively large amount of Ca is dissolved as the molten salt.  $\text{CaCl}_2$  has the melting point of about 780 °C, and the molten salt of  $\text{CaCl}_2$  is heated to at least the melting point thereof.

In the reactor cell 1, the molten  $\text{CaCl}_2$  which is of the molten salt is electrolyzed by passing the current between an anode electrode 2 and a cathode electrode 3, the  $\text{Cl}_2$  gas is generated on the side of anode electrode 2, and Ca is generated on the side of cathode electrode 3. The inside of the reactor cell 1 is divided into the anode electrode side and the cathode electrode side by a membrane 4. The membrane 4 is formed by a porous ceramic thin plate, and the membrane 4 blocks the movement of Ca generated on the side of the

cathode electrode 3 toward the side of the anode electrode 2 while permitting the molten salt to be moved.

In the reactor cell 1, the gaseous  $TiCl_4$  is injected in the dispersive manner into the molten salt on the cathode electrode side in the cell in parallel with the electrolysis of the molten salt. Therefore, the injected  $TiCl_4$  is reduced to generate the particulate metallic Ti by the Ca dissolved in the molten salt. The generated Ti particles move downward by the specific gravity difference and accumulate at the bottom on the cathode electrode side in the reactor cell 1.

[0049] The Ti particles accumulating at the bottom on the cathode electrode side of the reactor cell 1 are extracted from the reactor cell 1 along with the molten salt existing at the bottom of the reactor cell 1, and the Ti particles and the molten salt are sent to a Ti separation step. In the Ti separation step, the Ti particles and molten salt discharged from the reactor cell 1 are separated from the molten salt. Specifically the Ti particles are compressed to squeeze the molten salt. The Ti particles obtained in the Ti separation step is melted and formed in a Ti ingot.

On the other hand, the molten salt separated from the Ti particles in the Ti separation step is designated as the molten salt after use in which Ca is consumed to decrease the Ca concentration. The molten salt separated in the Ti separation step, along with other molten salt after use separately extracted from the reactor cell 1, is introduced to the anode electrode side in the reactor cell 1.

[0050] Ca in the molten salt is consumed on the cathode electrode side in the reactor cell 1 as the Ti particles are generated by the reducing reaction. However, Ca is generated near the surface of the cathode electrode 3 in the cell by the electrolysis which proceeds concurrently in the cell, and the consumed amount of Ca is replenished by Ca generated through the electrolysis. That is,  $TiCl_4$  supplied into the molten salt is sequentially reduced in a direct manner

by Ca generated near the surface of the cathode electrode 3.

On the other hand, the molten salt after use is sequentially introduced from the Ti separation step on the anode electrode side in the reactor cell 1. Therefore, a unidirectional flow of the molten salt is formed 5 from the anode electrode side toward the cathode electrode side in the reactor cell 1 to avoid the flow of Ca generated on the cathode electrode side into the anode electrode side. In the first embodiment mode shown in Fig. 2, the membrane 4 is provided to divide the inside of the reactor cell 1 into the anode electrode side and the cathode electrode side. The combination of the 10 provision of the membrane and the operation creating the unidirectional flow further effectively suppresses the back reaction and the decrease in the current efficiency caused thereby.

[0051] The  $\text{Cl}_2$  gas generated on the side of the anode electrode 2 in the reactor cell 1 is sent to a chlorination step. In the chlorination step, the  $\text{Cl}_2$  15 gas is caused to react with  $\text{TiO}_2$  and carbon (C) (chlorination) to generate  $\text{TiCl}_4$  which is of the Ti raw material. The generated  $\text{TiCl}_4$  is introduced to the reactor cell 1, and  $\text{TiCl}_4$  is used in a circulating manner to generate the Ti particles by the Ca reduction.

Thus, in the first embodiment mode, the Ti particle generation by the 20 Ca reduction, i.e., the Ca consumption and the Ca replenishment by the electrolysis are concurrently performed in the reactor cell 1. Therefore, it is not necessary to perform the Ca replenishment and Ca retrieval in the solid state, and the high-quality Ti particles can be produced continuously and 25 economically through the Ca reduction. The reactor cell 1 is used as both the reducing cell and the electrolytic cell, so that there is an economical advantage in the facilities. The flow of Ca generated on the cathode electrode side into the anode electrode side is avoided in the reactor cell 1, so that the back reaction in which Ca reacts with the  $\text{Cl}_2$  gas generated on the anode electrode side can be prevented.

The molten salt temperature is managed to be more than the melting point (about 780 °C) of CaCl<sub>2</sub> in each step.

[0052] Fig. 3 is a block diagram showing a Ti metal production apparatus to which a second embodiment mode of the present invention can be applied.

5        The second embodiment mode differs from the first embodiment mode in the following points. That is, a mixture of CaCl<sub>2</sub> and NaCl is used as the molten salt. In the mixture, CaCl<sub>2</sub> and NaCl are mixed together at a mixture ratio in which the melting point of the mixture becomes not more than 600 °C. The mixed molten salt is held at temperatures of not more than 600 °C in the  
10 reactor cell 1, and the mixed molten salt is held at temperatures of more than 600 °C in a separation cell 5 used in the Ti separation step.

[0053] Because the molten salt is held at temperatures of not more than 600 °C the reactor cell 1 in which the reducing reaction and the electrolytic reaction concurrently occur (namely, low-temperature reduction and  
15 low-temperature electrolysis are performed), Ca which is of the reducing agent exists in the molten salt (see chemical formula (d)), even if the molten salt is the mixed molten salt of CaCl<sub>2</sub> and NaCl. Therefore, the reducing reaction by Ca and the Ca generation and replenishment by the electrolysis are concurrently performed. The low-temperature reduction and the  
20 low-temperature electrolysis are performed in the reactor cell 1, so that the reactor material life can be lengthened to decrease the reactor material cost.

Because Ca has the higher reactivity than that of Mg, the development of the reactor material which can withstand Ca for a long period is the important technological problem in the mass production of Ti or Ti alloys.  
25        The molten salt temperature is decreased to reduce the impact on the reactor material during the operation by the low-temperature reduction and the low-temperature electrolysis, so that the present invention largely contributes to solve the problem of the reactor material life.

[0054] On the other hand, in the Ti separation step, the molten salt and the

Ti particles are extracted from the reactor cell 1 into the separation cell 5, or the molten salt is independently extracted from the reactor cell 1 into the separation cell 5. The molten salt extracted from the reactor cell 1 is already used, and the molten salt contains the slight amount of unreacted Ca although 5 Ca is consumed. When the molten salt containing the unreacted Ca is returned to the side of the anode electrode 2 in the reactor cell 1, the unreacted Ca reacts with the Cl<sub>2</sub> gas generated on the side of the anode electrode 2 to generate the back reaction.

However, in the second embodiment mode, unlike the reactor cell 1, 10 the molten salt is held at temperatures of more than 600 °C in the separation cell 5, so that the unreacted Ca slightly contained in the molten salt is replaced by Na (see chemical formula (e)). Unlike Na, Ca is not dissolved in the molten salt, Ca is separated to float on the molten salt, and Ca is removed from the molten salt. The molten salt in which the unreacted Ca (namely, reducing 15 agent metal) is removed is sent to the side of the anode electrode 2 in the reactor cell 1, and the molten salt temperature is managed to be not more than 600 °C. Because Na is removed as described above, the reaction of the chemical formula (d) does not occur, and Ca is not regenerated. Therefore, 20 the back reaction caused by the mixture of the unreacted Ca and the decrease in current efficiency caused by the back reaction are blocked.

[0055] That is, the Ti separation step in the second embodiment mode also functions as the Na separation step (reducing agent separation step), and the unreacted Ca in the molten salt returned to the reactor cell 1 is removed by previously replacing the unreacted Ca with Na, which enables the rational and 25 economical operation to be realized. Na separated from the molten salt in the separation cell 5 is sent back to the side of the cathode electrode 3 in the reactor cell 1, Na returns to Ca (see chemical formula (d)) by managing the melt at temperatures of not more than 600 °C, and Na is reused for the reducing reaction.

The molten salt temperature in the separation cell 5 can obviously be set at the same temperature as the reactor cell 1 whose temperature is not more than 600 °C. In this case, there is an advantage from the viewpoint of reactor material durability while the unreacted Ca cannot be removed.

5 [0056] Fig. 4 is a block diagram showing a Ti metal production apparatus to which a third embodiment mode of the present invention can be applied.

The third embodiment mode differs from the first embodiment mode in a structure of the cathode electrode 3. That is, the third embodiment mode is a configuration example of the Ti metal production apparatus in which the 10 production method described in (2) can be performed. The cathode electrode 3 is made of an electroconductive porous material in the third embodiment mode while the cathode electrode 3 is made of the solid metals such as Fe and Ti in the first embodiment mode. Specifically, the cathode electrode 3 is made of the electroconductive porous material such as a Ti sintered porous material and a 15 Fe sintered porous material. In the third embodiment mode, the  $TiCl_4$  gas which is of the Ti raw material is supplied into the molten salt on the side of the cathode electrode 3 in the reactor cell 1 through the porous cathode electrode 3 (namely, flows through the inside of the porous material).

[0057] In the case where  $TiCl_4$  is supplied into the molten salt on the cathode 20 electrode side in the reactor cell 1, it is necessary that  $TiCl_4$  is supplied to a portion near the surface of the cathode electrode 3 as much as possible. Because the Ca generation by the electrolysis is performed near the surface of the cathode electrode 3, the reaction efficiency is increased when  $TiCl_4$  is supplied to the portion near the surface of the cathode electrode 3. The 25 productivity of the Ti particles is further improved by adopting the third embodiment mode.

In the third embodiment mode, similarly to the second embodiment mode, the mixed molten salt of  $CaCl_2$  and  $NaCl$  can be used, the low-temperature reduction and low-temperature electrolysis can be performed

with the mixed molten salt of  $\text{CaCl}_2$  and  $\text{NaCl}$ , and the unreacted Ca (reducing agent) can be separated at high temperatures.

[0058] In the first to third embodiment modes, carbon or graphite is used as the anode electrode 2 to generate the  $\text{Cl}_2$  gas.

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#### INDUSTRIAL APPILCABILITY

[0059] According to the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, the feed rate of  $\text{TiCl}_4$  which is of the raw material can be enhanced, and the high-purity Ti or Ti alloys can 10 continuously be produced. In the reactor cell, the reducing reaction and the electrolytic reaction can concurrently be caused to proceed, and Ca consumed in the reducing reaction can be replenished by the electrolytic reaction, so that it is not necessary to singly handle Ca. The back reaction caused by Ca can also effectively be suppressed.

15 Accordingly, the method according to the present invention can effectively be utilized as means for efficiently and economically producing the high-purity Ti metals or Ti alloys, and the method according to the present invention can widely applied to the industrial Ti or Ti alloy production method.